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Anionic N-heterocyclic carbenes by decarboxylation of sydnone-4-carboxylates

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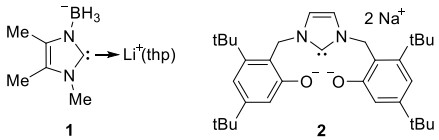
ABSTRACT

Unstable N-heterocyclic carbenes can be masked and stabilized as pseudo-cross-conjugated hetarenium-carboxylates which decarboxylate on warming. This study deals with the decarboxylation of carboxylates of mesoionic compounds to generate anionic N-heterocyclic carbenes. Lithium sydnone-4-carboxylates were therefore prepared via 4-bromosydnones by halogen-lithium exchange with nBuLi and subsequent treatment with carbon dioxide. Protonation gave the corresponding sydnone-4-carboxylic acids. Thermogravimetric measurements in addition to temperature dependent IR spectroscopy proved the decarboxylation of lithium sydnone-4-carboxylates and formation of the corresponding sydnone anions which can be represented as anionic N-heterocyclic carbenes. In DMSO-d_6 solution, water favors the decarboxylation. Calculations have been performed to elucidate the mechanism of the decarboxylation in the absence and presence of water.

1. Introduction

In the past years anionic N-heterocyclic carbenes (anionic NHC) have risen from laboratory curiosities to an innovative emerging field. Consequently, recent results concerning chemistry, properties and applications have been summarized in a first comprehensive review.[1] Anionic N-heterocyclic carbenes can be tripolar zwitterionic or anionic π-conjugated. For example, the N-heterocyclic carbene **1** bearing a borate at N1 is a zwitterionic anionic N-heterocyclic carbene.[2] Its negative charge is not in π-conjugation with the heterocycle (Scheme 1). Borate ligands can also be joined to the 4-position of imidazol-2-ylidene,[3] to the 2-position of imidazol-4-ylidene,[4] or to two N1 positions of two imidazol-2-ylidenes which form a B-bridged biscarbene.[5]

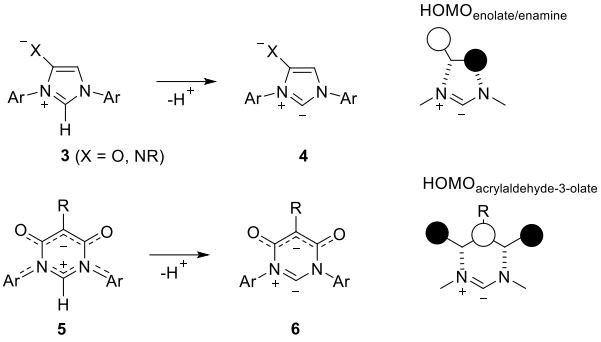


Scheme 1. *Examples of zwitterionic anionic N-heterocyclic carbenes.*

Aluminates,[6] gallates,[7] and other species also belong to this type of N-heterocyclic carbenes. Carbenes with one or more coordinating tethered anionic ligands such as **2** can also be termed zwitterionic anionic N-heterocyclic carbenes, because the sp^3-hybridized carbon atoms interrupt the conjugation between carbene and anionic moieties.[8]

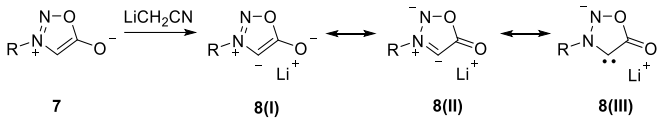
In order to generate conjugated anionic N-heterocyclic carbenes, it has been shown that mesomeric betaines are suitable starting materials. Application of Ramsden´s betaine classification theory[9] leads to several subclasses of conjugated anionic N-heterocyclic carbenes. A review summarizes knowledge which has been gained to date.[10] Thus, the deprotonation of mesoionic compounds such as imidazolium olate **3** (X = O)[11] or imidazolium aminide **3** (X = N)[12] give π-conjugated anionic N-heterocyclic carbenes such as **4**. Other examples have been described.[13] In these systems, the HOMO is joined to the diaminocarbene partial structure through an active atomic orbital coefficient. Cross-conjugated anionic N-heterocyclic carbenes such as **6** have been prepared from Kappe´s betaine **5** by deprotonation.[14] In carbene **6** the diaminocarbene moiety is joined to the anionic backbone through phase inversions (nodal positions; inactive positions) of the corresponding HOMO which cause a π-electronic charge-

separation in the ground state.[15] Thus, systems such as **6** have to be distinguished from the former mentioned species.



Scheme 2. *Anionic N-heterocyclic carbenes of mesomeric betaines.*

The anions **8(I) – 8(III)** of sydnones **7** (1,2,3-oxadiazolium-5-olates[16]) delocalize their negative charge within the π-conjugated system.[17] They can be represented as abnormal anionic N-heterocyclic carbenes **8(I)**, anionic normal N-heterocyclic carbenes **8(II)** and as electron sextet structures **8(III)**. Thus, sydnone anions, which proved to be quite stable as lithium adducts under exclusion of moisture,[17] are elements of the intersection of the compound classes of mesomeric betaines and anionic N-heterocyclic carbenes. They have been applied in synthetic chemistry[18] and as ligands of catalysts for Suzuki-Miyaura reactions under various conditions.[19] Sydnone imine carbenes have been described recently.[20] According to a very recently introduced quantitative analysis of factors influencing the ease of formation of oxa- and thia-N-heterocyclic carbenes, N-phenyl-sydnone has a CREF (carbene relative energy of formation) index value of 0.572 which is between the values of **3** (Ar = Ph; 0.600) and **5** (Ar = Me; 0.547).[21]



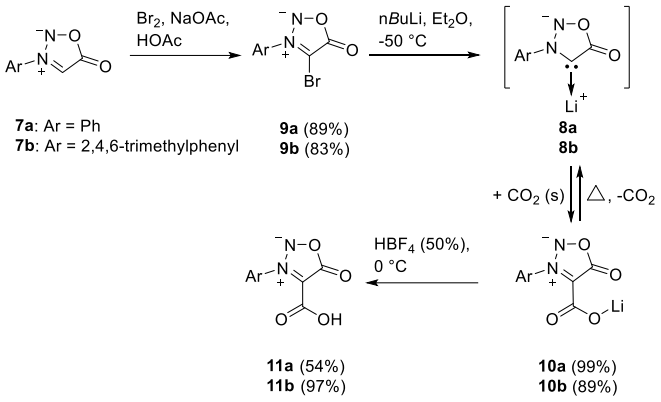
Scheme 3. *Selected canonical forms of sydnone anions.*

In continuation of our studies we became interested in sydnone-4-carboxylates, because a number of hetarenium-carboxylates can behave as masked N-heterocyclic carbenes. Examples are carboxylates of pyridin-2-ylidene derivatives,[22] imidazol-2-ylidenes,[23] pyrazolium-3-ylidenes,[24] and indazolium-3-ylidenes[25]. They were proven to be versatile starting materials for their *in-situ* generation by thermal decarboxylation which is a valuable alternative to deprotonations. Based on these reported developments and our finding that sydnone-4-carboxylates are effective additives for Suzuki-Miyaura reactions in acid,[19] we investigated the decarboxylation and the thermal behavior of sydnone-4-carboxylates in the solid state, in solution, and under ESI mass spectrometric conditions. The mechanism of the decomposition was also examined via DFT computations.

2. Results and discussion

2.1. *Syntheses and characterizations of sydnone-4-carboxylates*

Lithium sydnone-4-carboxylates **10a**,**b** were prepared by bromination at the C4 positions of the sydnones **7a**,**b** based on literature procedures to yield **9a**[26] and **9b**[27]. This was followed by bromine-lithium exchange and treatment of the resulting species with carbon dioxide. The formed sydnone-4-carboxylate **10a** has already been described in the literature before.[28] Finally, the lithium-carboxylates were protonated to give the carboxylic acids **11a,b**. In contrast to the generally applied procedures,[19,29] hydrochloric acid was replaced by hydrogen tetrafluoroborate as protonating agent in order to obtain better yields.



Scheme 4. *Synthesis of sydnone-4-carboxylic acids*.

We performed single crystal X-ray analyses on the isolated compounds **7a** and **7b**. We found, that the sydnone moiety and the aryl ring at position N3 are twisted by 104.7 ° (**7a**)[30] and 178.9 ° (**7b**)[17] from the molecular plane. In addition, single crystals of N-phenylsydnone-4-carboxylic acid **11a** were grown through slow evaporation of a concentrated solution in ethanol. The monoclinic crystals comprised neither water of crystallization nor solvent molecules (Fig. 1).

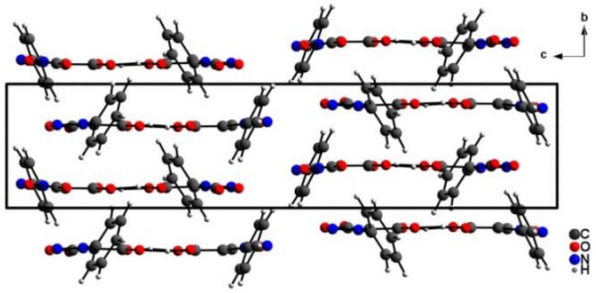


Figure 1. *Unit cell of single crystals of N-phenylsydnone-4-carboxylic acid* **11a**.

In the crystallized form, the N-phenylsydnone-4-carboxylic acid **11a** forms dimers which are connected *via* two relatively stable[31] homo-intermolecular hydrogen bonds[32] (Fig. 2).

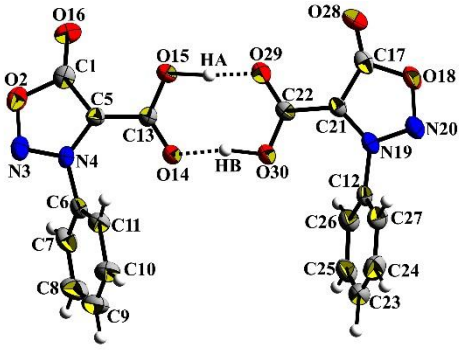
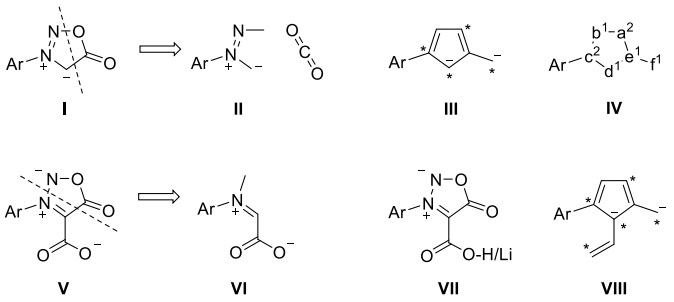


Figure 2. *Molecular drawing of N-phenylsydnone-4-carboxylic acid* **11a** *in the unit cell.*

According to the single crystal analysis, the torsion angle between the sydnone ring and the N3-aryl ring (C12-C10-N3-N2) is 116.0° and the dihedral angle between sydnone and carboxylate group (C5-C4-C7-O9) was measured to be 174.4°. The bond between the carboxylic acid moiety and the sydnone ring (1.44 Å) appears to be longer than in aliphatic carboxylic acids. The carbonyl double bond C7=O has a length of 1.23 Å. The bond length between the carbonyl carbon atom and the hydroxyl group is shortened (1.34 Å), caused by the dimeric structure.[33]

2.2.1 Classifications

Sydnones (**I**) are conjugated mesomeric betaines (CMB) constructed of the 1,3-dipole azomethin-imine (**II**) and carbon dioxide (Scheme 5). Their isoconjugated equivalents are even, non-alternant hydrocarbon dianions **III**. Mesoionic compounds of type A such as sydnones are constructed of atoms a-f which contribute electrons to the system as indicated by the superscripts (**IV**). Sydnone-4-carboxylates are anionic tripoles, therefore they are exceptions to the definition of mesomeric betaines in the classical sense.[34] Nevertheless they can be described as hybrids of the conjugated mesomeric betaines sydnone and the pseudo-cross-conjugated mesomeric betaines (PCCMB), because they possess the characteristic structural motif of 2-iminio-carboxylate **VI**. As mentioned before, this is also present in other masked N-heterocyclic carbenes.[22-25] In the carboxylic acids and their lithium salts (**VII**) the general type of conjugation does not change as they represent a vinylogous prolongation of the π-conjugated system of sydnones through a starred position of the isoconjugated hydrocarbon equivalent (**VIII**).



Scheme 5. *Architecture of sydnones, sydnone-4-carboxylates and lithium sydnone-4-carboxylates.*

2.2. *Decarboxylations*

In order to study the decarboxylation of sydnone carboxylates in the solid state, we first performed thermogravimetric analysis (TGA) measurements of the lithium sydnone-4-carboxylates **10a** and **10b**. In the case of **10a**, a slight weight loss could be observed between approximately 50 °C up to 205 °C which can be attributed to the release of approximately 0.2 mol of CO_2 under these conditions. At higher temperatures (above 205°C) the compound decomposed. In contrast, a weight loss in the range between 50°C and 83°C can be observed on measuring the lithium sydnone-4-carboxylate **10b** which can be attributed to the loss of approximately 2.3 mol of water of crystallization. Considering that no decarboxylation expected to take place under these conditions, the release of approximately 0.3 mol of CO_2 in the temperature range between 83°C and 198°C can be estimated.

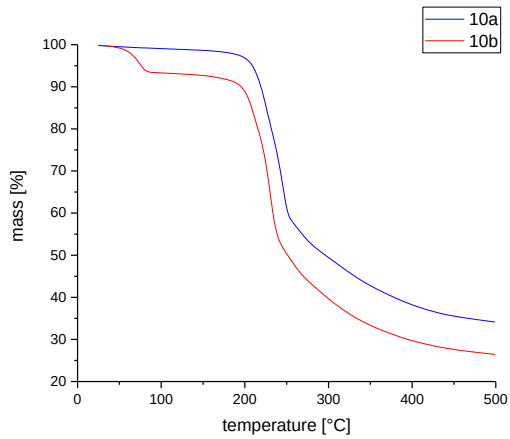


Figure 3. *TGA measurements of* **10a** *and* **10b**.

To prove the formation of CO_2 on heating the solids **10a,b** we performed vibrational spectroscopy in a wide temperature range. The decarboxylation was initiated by heating the KBr pellet on a Linkam table. The IR spectra of **10a** and **10b** are shown in figures 4 and 5, respectively.

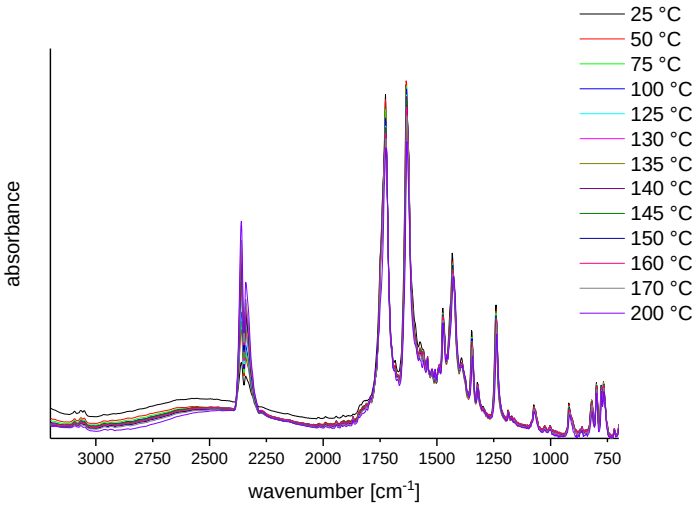


Figure 4. *IR spectra of* **10a** *at various temperatures, 25°C – 200°C.*

The absorbance bands at 2340-2400 cm^{-1} and 659 cm^{-1}, which increase on heating the lithium sydnone-4-carboxylate **10a** were identified as deformation vibrations of the released CO_2. We considered that this carbon dioxide was trapped within the KBr pellet and thus also could undergo recarboxylations of the sydnone carbene. Parallel to the CO_2 formation, the absorption bands at 1750 cm^{-1} and 1605 cm^{-1}, attributable to the asymmetric stretching vibration of the carboxylate group,[35] decreased and a new absorption band at 1646 cm^{-1} is formed. As the C(4)–H out-of-plane vibration absorbance band at 930 cm^{-1} as well as the vibration absorbance band at 3100 cm^{-1} of the sydnone **7a** could not be observed, the reprotonation under the applied measurement conditions appears to be negligible. In Figure 5 we compared the room temperature IR spectra of **7a** and **10a** to the IR spectra of **10a** at 200°C. The CO_2 bands, which are observable in the spectra measured at 25°C, are due to CO_2 from the atmosphere as the measurements were performed under air. After more than 3 hours at 200°C the sample decomposed.

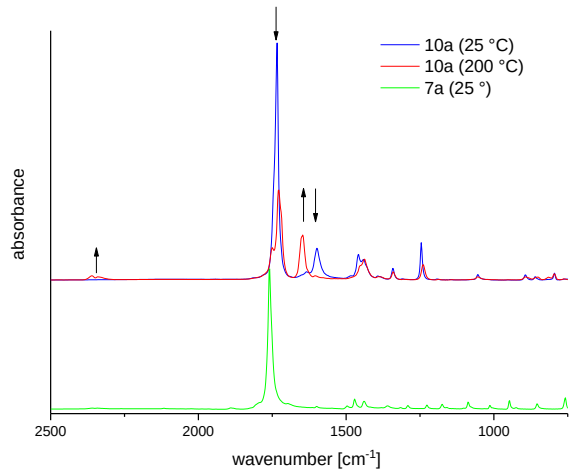


Figure 5. *IR spectra of* **7a** *and* **10a** *at 25 °C and* **10a** *at 200°C after heating for 5 minutes.*

The lithium sydnone-4-carboxylate **10b** behaved similarly (Figure 6). In the range of 1580-1800 cm^{-1} the absorbance bands of the carboxylate group at 1750 cm^{-1} and 1600 cm^{-1} disappeared on warming, while the absorption band at 1650 cm^{-1} increased. Neither the characteristic C(4)–H out-of-plane vibration of the sydnone **7b** at 930 cm^{-1} nor the vibration band at 3100 cm^{-1} were visible.

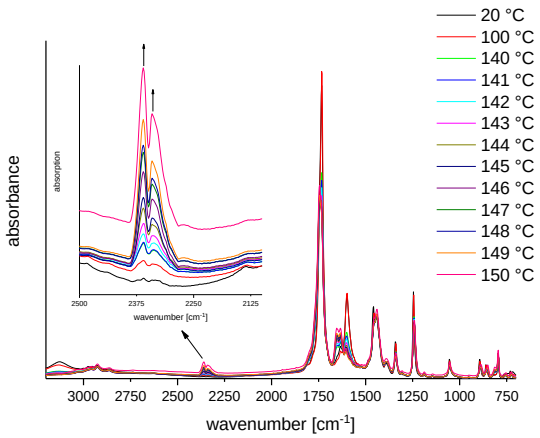


Figure 6. *IR spectra of* **10b** *at various temperatures, 20°C – 150°C.*

Low resolution electrospray ionization mass spectra were measured of methanolic solutions of the samples which were sprayed from acetonitrile in the anion detection mode. They displayed the [2 x **8a** - Li]$^-$ peak at *m/z* (%) = 329.0 (50 %), and the peaks of the non-associated sydnone anion [**8b**]$^-$, of [2 x **10b** -Li]$^-$, and of [5 x **10b** - Li]$^-$ at *m/z* = 203.1 (100%), 501.0 (55%), and 1263.2 (15%), respectively, so that in both cases the anionic N-heterocyclic carbene is detectable. This is also confirmed by high resolution mass spectrometry. The sydnone anion **8a** was identified by its peak at *m/z* = 161.0359 (calcd 161.0357), and the existence of **8b** under these conditions was verified by its peak at *m/z* = 203.0814 (calcd 203.0814). In the absence of lithium, the sydnone-4-carboxylates fragmented even at 0 V fragmentor voltage. HRESI-MSMS measurements reveal that the first step of the fragmentation, in both cases, is the decarboxylation to the sydnone anions **8a,b**. After that, the sydnone rings fragmented similarly as described for sydnones, as peaks at *m/z* = 131.1345 and *m/z* = 173.0356 were detectable, respectively.[36]

Next, we focused our investigations on decarboxylations in solution. Surprisingly, no decarboxylation was observed by ^{1}H NMR spectroscopy at increasing temperatures when anhydrous DMSO-d_6 was used as solvent. The spectra of lithium sydnone-4-carboxylate **10a** in wet DMSO-d_6 are shown in Figure 7. At 50°C compound **10a** decarboxylated within a couple of hours to the corresponding sydnone **7a**, with a notable induction period at the beginning. Analogously, we observed the formation of **7b** from lithium sydnone-4-carboxylate **10b** under these conditions.

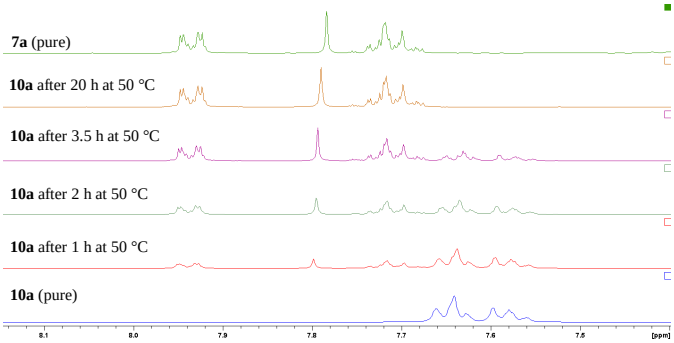


Figure 7. *Decarboxylation / reprotonation of* **10a** *at 50°C in DMSO-d_6, observed at 400 MHz and a measuring temperature of 25 °C.*

To gain insight into the mechanism of the decarboxylation, we performed DFT computations on the investigated system (for computational details, see Supporting Information). First, we calculated several structures of the contact ion pair complexes (CIPC) of lithium sydnone-4-carboxylate **10a** (Fig. 8.). We found that the anion is not planar due to steric interaction between the phenyl ring and the carboxyl group; in the most stable structure (**10a-I**), the torsion of the phenyl ring is -52.7°. The results suggest that the energetically favored position of the lithium cation is between the carboxylate oxygen and the exocyclic oxygen atoms. This is in accordance with IR spectroscopic observations, where red shifts of exocyclic CO stretching can be explained by the interaction of the oxygen with the lithium.[37]

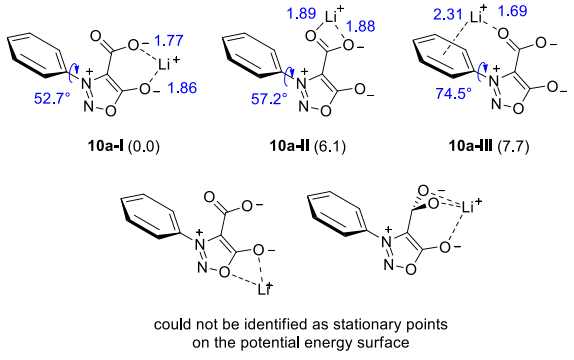


Figure 8. *Investigated contact ion pair structures of* **10a**. *Selected interatomic distances (in Å units) and torsion angles are shown in blue. Relative free energy values in kcal/mol units are collected in brackets.*

At this position, the positively charged lithium induces electron transfer from the electron rich C(4) atom towards the carboxylate and strengthens the C-C bond between them.[38]

The free energy barrier height of the decarboxylation of the CIPC is estimated to be 32.4 kcal/mol, and this process is predicted to be highly endergonic (27.5 kcal/mol).[39] However, the observed decarboxylation occurs in wet DMSO solvent media, which can allow the dissociation of the CIPC. We thus investigated the decarboxylation of the free anion as well. The influence of the presence of water on the energetics was evaluated through optimized structures and transition states with one or two coordinated water molecules.

In the absence of water molecules, the electronic energy of the anion increases gradually with the C-C distance and no local maximum could be identified. Nevertheless the calculated reaction free energy is significantly lower (14.4 kcal/mol), which suggests a more feasible pathway for the decomposition. In the presence of one coordinated water molecule, a transition state could be found; activation free energy on this reaction route is only 27.7 kcal/mol (Figure 9.). According to our computations additional water coordination is not beneficial to the reaction, because the barrier in the presence of two water molecules is slightly larger (28.4 kcal/mol).

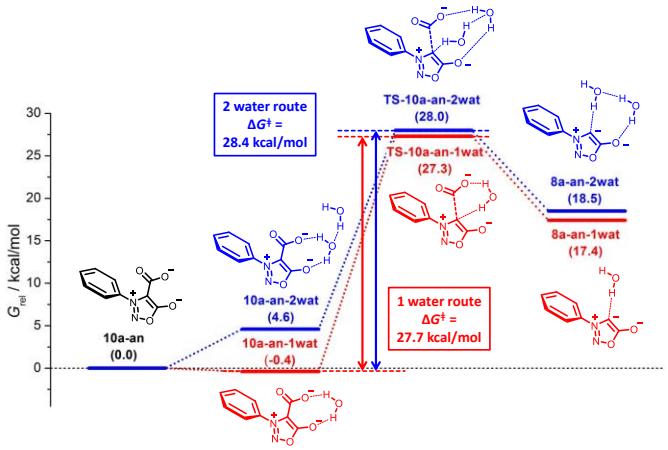


Figure 9. *Water assisted decarboxylation routes investigated computationally.*

As the decarboxylation requires the formation of an electron rich carbene, the stabilization of this state might facilitate the C-C bond cleavage. This is fully consistent with the obtained transition state structures, where stabilizing interaction can be observed between an OH and the C(4) atom (Figure 10).

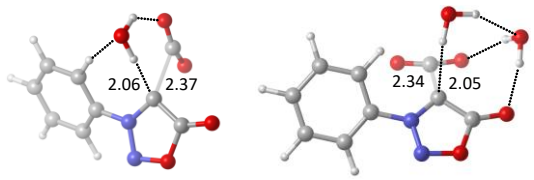


Figure 10. *Calculated decomposition transition states with the assistance of one water molecule (left) and two water molecules (right). Relative Gibbs free energy values (with respect to separated anion and water state) in kcal/mol units are shown in brackets. Selected C-C and C-HO distances are shown in Å units.*

These computational results suggest that the wet DMSO plays double role in the decomposition process in solution: (a) it allows the dissociation of the salt (b) and stabilizes the formed carbene via coordinated water molecules.

To complete our studies we also performed TGA measurements of the sydnone-4-carboxylic acids **11a,b** (Figure 12.). The decomposition of the sydnone carboxylic acids **11a,b** occurs under milder conditions in comparison to the sydnone-4-carboxylates, *i.e.* at 175°C (**11a**) and 180°C (**11b**). The small temperature range in which the decompositions were taking place is also striking. **11b** decomposes very rapidly above 203°C. The temperature is in the range of those which also shows the carboxylate **10b**, Figure 4. However, the decomposition of the acid proceeds in a smaller temperature range. In comparison with the corresponding lithium sydnone carboxylates, the sydnone carboxylic acids are more volatile.

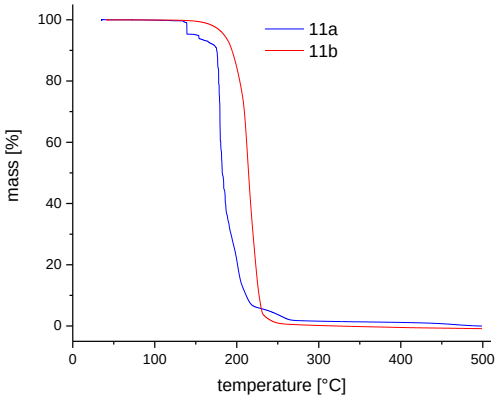


Figure 12. *TGA measurements of **11a** and **11b**.*

3. Conclusion

Anionic sydnone carbenes are formed by decarboxylation of sydnone-4-carboxylic acids in the solid state, in solution, and in the gas phase as evidenced by temperature-dependent IR spectroscopy, NMR spectroscopy in wet DMSO-d_6, and by ESI mass spectrometry, respectively. In solution, the presence of water facilitates the decarboxylation. This is in contrast to the carboxylates of other mesomeric betaines in which water is considered as a stabilizer. Computational analysis indicated that the lithium ion stabilizes the molecule and that one molecule of water is necessary to initiate the decarboxylation. The decarboxylation of sydnone-4-carboxylates supplement our knowledge concerning pseudo-cross-conjugated partial structures of mesomeric betaines as masked N-heterocyclic carbenes.

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4. Experimental Section

4.1. General considerations

The reactions were carried out under an atmosphere of nitrogen in oven-dried glassware. Nuclear magnetic resonance (NMR) spectra were obtained with a Bruker Avance 400 and Bruker Avance III 600 MHz. ^{1}H NMR spectra

were recorded at 400 MHz or 600 MHz. ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz, with the solvent peak or tetramethylsilane used as the internal reference. Multiplicities are described by using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet, and the signal orientations in DEPT experiments were described as follows: o = no signal; + = up (CH, CH_3); - = down (CH_2). FT-IR spectra were obtained on a Bruker FT-IR-Raman-spectrometer, Vertex 70 V, in the range of 400 to 4000 cm^{-1}. A Linkam-table was connected to the IR device which used to heat the KBr-pellets. ATR-IR spectra were obtained on a Bruker Alpha in the range of 400 to 4000 cm^{-1}. The mass spectra were measured with a Varian 320 MS Triple Quad GC/MS/MS with a Varian 450-GC. The electrospray ionization mass spectra (ESIMS) were measured with an Agilent LCMSD series HP 1100 with APIES. The compound samples were sprayed from MeCN at 4000 V capillary voltage and fragmentor voltages of 30 V, unless otherwise noted. The HR-MS spectra were obtained with a Bruker Impact II or with a Bruker Daltonik Tesla-Fourier transform-ion cyclotron resonance mass spectrometer with electrospray ionization, or a Waters Micromass LCT with direct inlet. Melting points are uncorrected and were determined in an apparatus according to Dr. Tottoli (Büchi). Yields are not optimized. The TGA measurements were taken with a Q5000 IR from TA Instruments at a heating rate of 10 °C/ min and nitrogen as the purge gas. All density-functional theory (DFT)-calculations were carried out by using Gaussian09 software.

X-Ray structure analysis of 11a, M = 206.16 g mol^{-1}: A suitable single crystal of **11a** was selected under a polarization microscope and mounted in a glass capillary (d = 0.3 mm). The crystal structure was determined by X-ray diffraction analysis using graphite monochromated Mo-K_α radiation (0.71073 Å) [T = 123(2) K], whereas the scattering intensities were collected with a single crystal diffractometer (STOE IPDS II). The crystal structure was solved by Direct Methods using SHELXS-97 and refined using alternating cycles of least squares refinements against F^2 (SHELXL-97). All non-H atoms were located in Difference Fourier maps and were refined with anisotropic displacement parameters. The H positions were determined by a final Difference Fourier Synthesis.[40]

11a crystallized in the monoclinic space group $P2_1/c$ (no. 14), lattice parameters a = 10.242(2) Å, b = 6.233(1) Å, c = 27.783(5) Å, β = 94.65(2)°, V = 1767.8(6) Å^3, Z = 8, $d_{calc.}$ = 1.549 g cm^{-3}, F(000) = 848 using 3270 independent reflections and 319 parameters. $R1$ = 0.0719, $wR2$ = 0.1388 [$I > 2\sigma(I)$], goodness of fit on F^2 = 1.059, residual electron density 0.241 and –0.253 e Å^{-3}.

Further details of the crystal structure investigations have been deposited with the Cambridge Crystallographic Data Center, CCDC 1815512. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44(1223)-336 033; e-mail: **fileserv@ccdc.ac.uk** or **http://www.ccdc.cam.ac.uk**).

4.1.1. 4-Bromo-N-phenylsydnone 9a

A sample of 2.50 g (15.4 mmol) of N-phenylsydnone were treated with 2.70 g (32.9 mmol) of anhydrous sodium acetate and then with 9 mL of glacial acetic acid. Then, 2.46 g (0.79 mL, 15.4 mmol) bromine was dissolved in 9 mL of glacial acetic acid and added dropwise under vigorous stirring to the mixture of sydnone and NaOAc in AcOH. After stirring for 1 h at rt the reaction mixture was poured on 400 mL of ice and water, and then the crude product was extracted with dichloromethane. The organic phase was separated, washed subsequently with 10% of sodium thiosulfate in water, 30 mL of brine, and finally with 10% of $NaHCO_3$ in water. The organic phase was dried over $MgSO_4$, evaporated and the crude product was recrystallized from ethanol. Yield: 3.32 g (89%). ^{1}H NMR (600 MHz, DMSO-d$_6$): δ = 7.61–7.70 (m, 4 H, 2‘-*H*C+3‘-*H*C+4‘-*H*C+5‘-*H*C), 7.71–7.75 (m, 1 H, 4‘-*H*C). ^{13}C NMR (150 MHz, DMSO-d$_6$): δ = 85.2 (*C*-4, $^1J_{CC}$ = 99.6 Hz), 129.6 (H*C*-2‘+H*C*-6‘), 130.0 (H*C*-3‘+H*C*-5‘), 134.11 (H*C*-4‘), 142.7 (*C*-1‘), 165.8 (*C*-5, $^1J_{CC}$ = 85.6 Hz) ppm. ^{15}N NMR (61 MHz, DMSO,d6): δ = -35.4 (*N*-2), -100.7 (*N*-3) ppm.[26]

4.1.2. 4-Bromo-N-mesitylsydnone 9b

This compound was prepared in analogy to **9a**. A sample of 1.0 g (4.9 mmol) of N-mesitylsydnone, 0.40 g (4.9 mmol) of NaOAc, 0.78 g (0.25 mL, 4.9 mmol) of bromine, and 5.8 mL of glacial acetic acid gave 1.15 g (83%) of 4-bromo-N-mesitylsydnone, mp.: 123 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.08 (s, 6 H, 1‘‘-H_3C+3‘‘-H_3C), 2.36 (s, 3 H, 2‘‘-H_3C), 7.23-7.24 (m, 2 H, 3‘-*H*C+5‘-*H*C) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.1 (H_3C-1‘‘+H_3C-3‘‘), 20.7 (H_3C-2‘‘), 86.7 (*C*-4), 129.6 (H*C*-3‘+H*C*-5‘), 133.9 (*C*-1‘+*C*-2‘+*C*-6‘), 142.4 (*C*-4‘), 165.1 (*C*-5) ppm. IR (ATR): ν = 2957, 2919, 1754, 1739, 1729, 1703, 1605, 1482, 1454, 1435, 1413, 1382, 1336, 1306, 1294, 1210, 1186, 1134, 1038, 1011, 975, 890, 853, 735, 714, 667, 595, 577, 538, 508, 497, 489, 465, 449, 428 cm^{-1}. MS (ESI, 30 V): m/z (%) = 589.0 (100) [2M+Na]$^+$. HRESI-MS: calc.: 304.9896 Da [M+Na]$^+$, meas.: 304.9902 Da [M+Na]$^+$.

4.1.3. Lithium N-phenylsydnone-4-carboxylate 10a

A sample of 0.10 g (0.4 mmol) of 4-bromo-N-phenylsydnone **9a** was suspended in 5 mL of diethyl ether, cooled to -50 °C and stirred at that temperature for approximately 30 min. Then, 0.2 mL (0.12 g) of nBuLi (23% in cyclohexane) was added dropwise carefully, and stirring was continued for 30 min. Finally, solid carbon dioxide was added rapidly. The ether was removed at rt with a continuous nitrogen flow and the resulting product was dissolved in distilled water. Then, the aqueous phase was washed subsequently with toluene, petroleum ether, ethyl acetate and dichloromethane, evaporated *in vacuo* at maximum 30 °C to dryness. Toluene was added and distilled off *in vacuo*. Finally, the product was dried *in vacuo* for 6 h without heating. Yield: 0.88 g (> 99%), dec > 220 °C (decarboxylation). ^{1}H NMR (400 MHz, DMSO,d$_6$): δ = 7.57–7.60 (m, 2 H, 2‘-*H*C +6‘-*H*C), 7.64–7.66 (m, 3 H, 3‘-*H*C+4‘-*H*C+5‘-*H*C)ppm. ^{13}C NMR (100 MHz, DMSO,d$_6$): δ = 107.1 (*C*-4), 125.5 (H*C*-3’+H*C*-5’ or H*C*-2’+H*C*-6’), 128.7 (H*C*-2’+H*C*-6’ or H*C*-3’+H*C*-5’), 131.2 (H*C*-4’), 135.4 (*C*-1’), 157.0 (*C*-7), 168.7 (*C*-5) ppm. IR (KBr): ν = 3094, 3068, 3051, 1839, 1723, 1633, 1519, 1494, 1473, 1441, 1422, 1388, 1345, 1322, 1237, 1187, 1172, 1116, 1073, 1027, 1013, 1003, 979, 919, 850, 817, 797, 777, 765, 719, 692, 673, 661, 646, 608, 523, 491, 458 cm^{-1}. MS (ESI, 100 V): m/z (%) = 329.0 (50) [2M-Li-2CO_2]. HRESI-MS: calc.: 161.0351 Da [M-Li-CO_2]$^-$, meas.: 161.0355 Da [M-Li-CO_2].

4.1.4. Lithium N-mesitylsydnone-4-carboxylate 10b

The product was prepared under analogous reaction conditions. A sample of 0.20 g (0.4 mmol) of 4-bromo-N-mesitylsydnone in 15 mL of diethylether (abs.) with 0.3 mL (0.20 g, 0.6 mmol) of nBuLi (23% in hexane) gave 0.17 g (95%). Dec. > 244 °C. ^{1}H NMR (400 MHz, DMSO,d$_6$): δ = 2.00 (s, 6 H, 1‘‘-H_3C+3‘‘-H_3C), 2.32 (s, 3 H, 2‘‘-H_3C), 7.07 (s, 2 H, 3‘-*H*C+5‘-*H*C) ppm. ^{13}C NMR (100 MHz, DMSO,d$_6$): δ = 16.3 (H_3C-1‘‘+H_3C-3‘‘), 20.6 (H_3C-2‘‘), 107.3 (*C*-4), 128.6 (H*C*-3‘+H*C*-5‘), 132.5 (*C*-1‘), 133.1 (*C*-2‘+*C*-6‘), 140.0 (*C*-4‘), 156.8 (*C*-7), 168.3 (*C*-5) ppm. IR (ATR): ν = 2923, 1805, 1739, 1602, 1456, 1440, 1393, 1338, 1307, 1240, 1191, 1145, 1052, 889, 860, 851, 825, 792, 751, 727, 684, 634, 599, 556, 476, 444, 422, 417, 413 cm^{-1}. MS (ESI, 50 V): m/z (%) = 211.1 (23) [M-CO_2+H]$^+$, 261.1 (100) [M+Li]$^+$, 509.0 (10) [2M+H]$^+$, 769.2 (43) [3M+Li]$^+$, 858.8 (33) [M+3(M-CO_2)+H]$^+$. MS (ESI, 30 V): m/z (%) = 203.1 (100) [M-Li-CO_2], 501.0 (55) [2M-Li]$^-$, 1263.2 (15) [5M-Li]$^-$. HRESI-MS: calc.: 271.0689 Da [M-Li+H+Na]$^+$, meas.: 271.0691 Da [M-Li+H+Na]$^+$, calc.: 203.0821 Da [M-Li-CO_2]$^-$, meas.: 203.0818 Da [M-Li-CO_2].

4.1.5 Lithium N-phenylsydnone-4-carboxylic acid 11a

A sample of 0.22 g (1.0 mmol) of lithium N-phenyl-sydnone-4-carboxylate was dissolved in distilled water and cooled to 0 °C in an ice bath. HBF_4 (50% in water) was added dropwise until pH 3. After stirring for 5 minutes, the solid was filtered off. The crude product was recrystallized from ethanol. Yield: 0.11 g (54%). Mp.: 202 °C (decarboxylation). ^{1}H NMR (400 MHz, DMSO,d$_6$): δ = 3.44 (br s, 1 H, O*H*), 7.62–7.66 (m, 2 H, 2‘-*H*C+6‘-*H*C or 3‘-*H*C+5‘-*H*C), 7.69–7.73 (m, 1 H, 4‘-*H*C), 7.76–7.78 (m, 2 H, 3‘-*H*C+5‘-*H*C or 2‘-*H*C+6‘-*H*C) ppm. ^{13}C NMR (100 MHz, DMSO,d$_6$): δ = 100.6 (*C*-4), 125.6 (H*C*-2’+H*C*-6’ or H*C*-3’+H*C*-5’), 129.1 (H*C*-3’+H*C*-5’ or H*C*-2’+H*C*-6’), 132.0 (*C*-4‘), 135.2 (*C*-1‘), 157.6 (*C*-7), 164.4 (*C*-5) ppm. IR (ATR): ν = 2899, 2861, 2840, 2765, 2718, 2693, 2653, 2616, 2589, 2554, 2539, 2503, 2483, 2460, 2445, 2432, 1805, 1769, 1670, 1654, 1649, 1611, 1483, 1459, 1414, 1401, 1366, 1325, 1307, 1210, 1177, 1160, 1059, 1026, 1001, 990, 977, 921, 903, 879, 842, 766, 758, 740, 727, 714, 685, 669, 663, 629, 607, 592, 518, 479, 437 cm^{-1}.

4.1.6 Lithium N-mesitylsydnon-4-carboxylic acid 11b

A sample of 0.8 g (3.0 mmol) of lithium N-phenyl-sydnone-4-carboxylate was dissolved in distilled water and cooled to 0 °C in an ice bath. HBF_4 (50% in water) was added dropwise until pH 3. After stirring for 5 minutes the solid was filtered off. The crude product was recrystallized from ethanol. Yield: 0.73 g (97%). Mp.: 203 °C (decarboxylation). ^{1}H NMR (400 MHz, MeOD,d$_4$): δ = 2.11 (s, 6 H, 1‘‘-H_3C+3‘‘-H_3C), 2.39 (s, 3 H, 2‘‘-H_3C), 7.13 (s, 2 H, 3‘-*H*C+5‘-*H*C) ppm. ^{13}C NMR (100 MHz, MeOD,d$_4$): δ = 16.7 (H_3C-1‘‘+H_3C-3‘‘), 21.2 (H_3C-2‘‘), 101.8 (*C*-4), 130.3 (H*C*-3’+H*C*-5’), 133.3 (*C*-1’), 134.9 (*C*-2’+*C*-6’), 143.5 (*C*-4’), 159.0 (*C*-7), 166.9 (*C*-5) ppm. MS (ESI, 30 V): m/z (%) = 271.0 (100) [M+Na]$^+$, 293.0 (23) [M-H+2Na]$^+$, 519.2 (15) [2M+Na]$^+$, 541.2 (35) [2M-H+2Na]$^+$. IR (ATR): ν = 2986, 2960, 2916, 2849, 2711, 2662, 2600, 2567, 2514, 1806, 1687, 1683, 1660, 1605, 1471, 1389, 1390, 1366, 1324, 1305, 1211, 1185, 1139, 1046, 980, 915, 893, 862, 846, 803, 761, 735, 715, 704, 680, 625, 598, 554, 480, 464, 446, 434 cm^{-1}. HRESI-MS: calc. 271.0695 Da [M+Na]$^+$, mears. 271.0695 Da [M+Na]$^+$.

5. References

1. A. Nasr, A. Winkler, M. Tamm, *Coord. Chem. Rev.* **2016**, *316*, 68 – 124.

2. A. Wacker, H. Pritzkow, W. Siebert, *Eur. J. Inorg. Chem.* **1998**, 843 – 849.
3. (a) A. R. Chianse, A. Kovacevic, B. M. Zeglis, J. W. Faller, R. H. Crabtree, *Organometallics* **2004**, *23*, 2461 – 2468. (b) S. Gründemann, A. Kovacevic, M. Albrecht, J. W. Faller, R. H. Crabtree, *J. Am. Chem. Soc.* **2002**, *124*, 10473 – 10481. (c) Y. Wang, M. Y. Abraham, R. J. Gilliard, P. Wei, J. C. Smith, G. H. Robinson, *Organometallics* **2012**, *31*, 791 – 793. (d) D. Holschumacher, T. Bannenberg, C. G. Hrib, P. G. Jones, M. Tamm, *Angew. Chem. Int. Ed.* **2008**, *47*, 7428 – 7432; *Angew. Chem.* **2008**, *120*, 7538 – 7542. (e) S. Kronig, E. Theuergarten, C. G. Daniliuc, P. G. Jones, M. Tamm, *Angew. Chem. Int. Ed.* **2012**, *51*, 3240 – 3244; *Angew. Chem.* **2012**, *124*, 3294 – 3298.
4. (a) A. Jana, R. Azhakar, G. Tavčar, H. W. Roesky, I. Objartel, D. Stalke, *Eur. J. Inorg. Chem.* **2011**, 3686 – 3689. (b) C. Pranckevicius, D. W. Stephan, *Chem. Eur. J.* **2014**, *20*, 6597 – 6602.
5. (a) R. Fränkel, J. Kniczek, W. Ponikwar, H. Nöth, K. Polborn, W. P. Fehlhammer, *Inorg. Chim. Acta* **2001**, *312*, 23 – 39. (b) I. Nieto, R. P. Bontchev, J. M. Smith, *Eur. J. Inorg. Chem.* **2008**, *2008*, 2476 – 2480.
6. (a) A.-L. Schmitt, G. Schnee, R. Weiter, S. Dagorne, *Chem. Commun.* **2010**, *46*, 2480 – 2482. (b) Y. Wang, Y. Xie, M. Y. Abraham, P. Wei, H. F. Schaefer, P. R. V. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2010**, *132*, 14370 – 14372.
7. M. Chen, Y. Wang, R. J. Gilliard, P. Wei, N. A. Schwartz, G. H. Robinson, *Dalton Trans.* **2014**, *43*, 14211 – 14214.
8. B. Lui, J. Zhao, C. Luo, F. Lu, S. Tao, Q. Tong, *J. Mater. Chem. C* **2016**, *4*, 2003 – 2010.
9. (a) C. A. Ramsden, *Tetrahedron* **2013**, *69*, 4146 – 4159. (b) C. A. Ramsden, W. P. Oziminski, *Tetrahedron* **2014**, *70*, 7158 – 7165. (c) W. P. Oziminski, C. A. Ramsden, *Tetrahedron* **2015**, *71*, 7191 – 7198.
10. A. Schmidt, S. Wiechmann, T. Freese, *ARKIVOC* **2013**, *i*, 424 – 469.
11. (a) L. Benhamou, N. Vujkovic, V. César, H. Gornitzka, N. Lugan, G. Lavigne, *Organometallics* **2010**, *29*, 2616 – 2630. (b) L. Benhamou, V. César, H. Gornitzka, N. Lugan, G. Lavigne, *Chem. Commun.* **2009**, 4720 – 4722. (c) A. T. Biju, K. Hirano, R. Fröhlich, F. Glorius, *Chem. Asian J.* **2009**, *4*, 1786 – 1789.
12. A. A. Danopoulos, K. Yu. Monakhov, P. Braunstein, *Chem. Eur. J.* **2013**, *19*, 450 – 455.
13. (a) N. Pidlypnyi, S. Wolf, M. Liu, K. Rissanen, M. Nieger, A. Schmidt, *Tetrahedron* **2014**, *70*, 8672 – 8680. (b) N. Pidlypnyi, J. C. Namyslo, M. H. H. Drafz, M. Nieger, A. Schmidt, *J. Org. Chem.* **2013**, *78*, 1070 – 1078. (c) N. Pidlypnyi, F. Uhrner, M. Nieger, M. H. H. Drafz, E. G. Hübner, J. C. Namyslo, A. Schmidt, *Eur. J. Org. Chem.* **2013**, *2013*, 7739 – 7748.
14. (a) G. Lavigne, V. César, N. Lugan, *Chem. Eur. J.* 2010, 16, 11432 – 11442. (b) V. César, N. Lugan, G. Lavigne, *J. Am. Chem. Soc.* **2008**, *130*, 11286 - 11287.
15. (a) K. T. Potts, P. M. Murphy, W. R. Kuehnling, *J. Org. Chem.* **1988**, 2889 – 2898. (b) K. T. Potts, P. M. Murphy, M. R. DeLuca, W. R. Kuehnling, *J. Org. Chem.* **1988**, 2898 – 2910.
16. (a) A.W. Brown, J. P. A. Harrity, *Tetrahedron* **2017**, *73*, 3160 – 3172. (b) A. W. Brown, J. Comas-Barceló, J. P. A. Harrity, *Chem. Eur. J.* **2017**, *23*, 5228 – 5231. (c) T. Wezeman, J. Comas-Barceló, M. Nieger, J. P. A. Harrity, S. Bräse, *Org. Biomol. Chem.* **2017**, *15*, 1575 – 1579. (d) D. L. Brown, J. P. Harrity, *Tetrahedron* **2010**, *66*, 553 – 568. (e) T. L. Gilchrist, *In Science of Synthesis*; R. C. Storr, T. L. Gilchrist, Ed.; Thieme Verlag: Stuttgart, Germany, **2004**, *Vol. 13*, pp. 109 - 125. (f) R. Chandrasekhar, M. J. Nanjan, *Mini-Rev. Med. Chem.* ***2012***, *12*, 1359 – 1365. (g) C. Wu, Y. Fang, R. C. Larock, F. Shi, *Org. Lett.* **2010**, *12*, 2234 – 2237. (h) S. K. Bhosalea, S. R. Deshpandeb, R. D. Waghc, *J. Chem. Pharm. Res.* **2015**, *7*, 1333 – 1343. (i) S. T. Asundaria, C. Pannecouque, E. de Clercq, K. C. Patel, *Pharm. Chem. J.* **2014**, *48*, 260 – 268.
17. S. Wiechmann, T. Freese, M. H. H. Drafz, E. G. Hübner, J. C. Namyslo, M. Nieger, A. Schmidt, *Chem. Commun.* **2014**, *50*, 11822 – 11824.
18. (a) S. N. Lebedev, I. A. Cherepanov, V. N. Kalinin, *Russ. Chem. Bull., Int. Ed.* **2002**, *51*, 899 – 900. (b) L. N. Morozova, L. S. Isaeva, P. V. Petrovskii, D. N. Kratsov, S. F. Min, V. V. Kalinin, *J. Organomet. Chem.* **1990**, *381*, 281 – 284. (c) V. N. Kalinin, F. M. She, V. N. Khandozhko, P. V. Petrovskii, *Russ. Chem. Bull. Int. Ed.* **2001**, *50*, 525 – 530.
19. (a) A.-L. Lücke, S. Wiechmann, T. Freese, A. Schmidt, *Synlett* **2017**, *28*, 1990 – 1993. (b) A.-L. Lücke, S. Wiechmann, T. Freese, Z. Guan, A. Schmidt *Z. Naturforsch.* **2016**, *71B*, 643 – 650.
20. T. Freese, A.-L. Lücke, C. A. S. Schmidt, M. Polamo, M. Nieger, J. C. Namyslo, A. Schmidt, *Tetrahedron* **2017**, *73*, 5350 – 5357.
21. C. A. Ramsden, W. P. Oziminski, *J. Org. Chem.* **2017**, *82*, 12485 – 12491.
22. (a) R. Breslow, *J. Am. Chem. Soc.* **1958**, *80*, 3719 – 3726. (b) K. W. Ratts, R. K. Howe, W. G. Phillips, *J. Am. Chem. Soc.* **1969**, *91*, 6115 – 6121. (c) H. Quast, E. Schmitt, *Liebigs Ann. Chem.* **1970**, *732*, 43 – 63. (d) A. R. Katritzky, H. M. Faid-Allah, *Synthesis* **1983**, 149 – 150. (e) D. Lavorato, J. K. Terlouw, T. K. Dargel, W. Koch, G. A. McGibbon, H. Schwarz, J. *Am. Chem. Soc.* **1996**, *118*, 11898 – 11904. (f) A. R. Katritzky, A. J. Cozens, A. Ossana, O. Rubio, N. Dabbas, *J. Chem. Soc., Perkin Trans. 1* **1985**, 2167 – 2172.
23. (a) M. Fèvre, J. Pinaud, A. Leteneur, Y. Gnanou, J. Vignolle, D. Taton, K. Miqueu, J.-M. Sotiropoulos, *J. Am. Chem. Soc.* **2012**, *134*, 6776 – 6784. (b) E. L. Kolychev, T. Bannenberg, M. Freytag, C. G. Daniliuc, P. G. Jones, M. Tamm, *Chem. Eur. J.* **2012**, *18*, 16938 – 16946. (c) T. K. Olszewski, D. E. Jasko´lska, *Heteroatom Chem.* **2012**, *23*, 605 – 609. (d) T. Le Gall, S. Baltatu, S. K. Collins, *Synthesis* **2011**, 3687 – 3691. (e) A. Rahimi, J. C. Namyslo, M. H. H. Drafz, J. Halm, E. Hübner, M. Nieger, N. Rautzenberg, A. Schmidt, *J. Org. Chem.* **2011**, *76*, 7316 – 7325. (f) X. Sauvage, G. Zaragoza, A. Demonceau, L. Delaude, *Adv. Synth. Catal.* **2010**, *352*, 1934 – 1948. (g) J. Li, J. Peng, G. Zhang, Y. Bai, G. Lai, X. Li, *New J. Chem.* **2010**, *34*, 1330 – 1334. (h) P. Bissinger, H. Braunschweig, T. Kupfer, K. Radacki, *Organometallics* **2010**, *29*, 3987 – 3990. (i) X. Sauvage, A. Demonceau, L. Delaude, *Adv. Synth. Catal.* **2009**, *351*, 2031 – 2038. (j) L. Tommasi, F. Sorrentino, *Tetrahedron Lett.* **2009**, *50*, 104 – 107. (k) A. Schmidt, A. Beutler, M. Albrecht, F. J. Ramírez, *Org. Biomol. Chem.* **2008**, *6*, 287 – 295.
24. (a) A. Schmidt, N. Münster, A. Dreger, *Angew. Chem.* **2010**, *122*, 2851 – 2854; *Angew. Chem. Int. Ed.* **2010**, *49*, 2790 – 2793. (b) A. Schmidt, A. Dreger, *Curr. Org. Chem.* **2011**, *15*, 2897 – 2970. (c) A. Schmidt, T. Habeck, *Lett. Org. Chem.* **2005**, *2*, 37 – 39.
25. (a) Z. Guan, M. Gjikaj, A. Schmidt, *Heterocycles* **2014**, *10*, 2356 – 2367. (b) Z. Guan, S. Wiechmann, M. Drafz, E. Hübner, A. Schmidt, *Org. Biomol. Chem.* **2013**, *11*, 3558 – 3567. (c) A. Schmidt, B. Snovydovych, S. Hemmen, *Eur. J. Org. Chem.* **2008**, *25*, 4313 – 4319. (d) A. Schmidt, L. Merkel, W. Eisfeld, *Eur. J. Org. Chem.* **2005**, 2124 – 2130.
26. a) J. C. Earl, *Recl. Trav. Chim. Pays-Bas* **1956**, *75*, 1080–1082. b) H. Kato, K. Nakahara, M. Ohta, *Nippon Kagaku Zasshi* **1956**, *77*, 1304 – 1306.
27. K. Turnbull, *J. Heterocycl. Chem.* **1985**, *22*, 965 – 968.
28. H. Kato, M. Ohta, *Bull. Chem. Soc. Jpn.* **1959**, *32*, 282 – 284.
29. D. Lavorato, J. K. Terlouw, T. K. Dargel, W. Koch, G. A. McGibbon, H. Schwarz, *J. Am. Chem. Soc.* **1996**, *118*, 11898 – 11904.
30. S. Nespurek, J. Hasek, M. Sorm, K. Huml, *J. Mol. Sturct.* **1982**, *82*, 95 – 105.
31. (a) A. Schmidt, S. Wiechmann, C. F. Otto in Scriven, Ramsden (Hrsg.) *Adv. Heterocycl. Chem.* **2016**, *119*, 143 – 172. (b) A. Schmidt, B. Snovydovych, J. Casado, J. J. Quirante, J. T. López Navarrete, F. J. Ramírez, *Phys. Chem. Chem. Phys.* **2009**, *11*, 341 – 348.
32. (a) G. R. Desiraju, *Acc. Chem. Res.* **1991**, *24*, 290 – 296. (b) G. R. Desiraju, *Acc. Chem. Res.* **1996**, *29*, 441 – 449. (c) T. Steiner, *Crystallogr. Rev.* **1996**, *6*, 1 – 51. (d) T. Steiner, *Chem. Commun.* **1997**, 727 – 734. (e) G. R. Desiraju, T. Steiner, *The Weak Hydrogen Bond in Structural Chemistry and Biology*, Oxford University Press, **1999**.
33. K. P. C. Vollhardt, N. E. Schore, H. Butenschön, *Organische Chemie*, 5. Edition, Wiley-VCH, Weinheim, **2011**, p. 936.
34. W. D. Ollis, S. P. Stanforth, C. A. Ramsden, *Tetrahedron* **1985**, *41*, 2239 – 2329.
35. (a) B. C. Smith, *Infrared spectral interpretation: a systematic approach*, 1. Edition, CRC Press LLC, Boca Raton, **1999**. (b) E. G. Palacios, A. J. Monhemius, *Hydrometallurgy* **2001**, *62*, 135 – 143.
36. R. C. Dougherty, R. L. Foltz, L. B. Kier, *Tetrahedron*, **1970,** *26*, 1989 – 2005.
37. M. G. Ezernitskaya, B. V. Lokshin, E. I. Kazimirchuk, V. K. Khandozhko, V. N. Kalinin, *Mikrochim. Acta, Suppl.* **1997**, *14*, 381-382.
38. We performed potential energy scan calculations for the decarboxylations varying the distance between the carbene and carboxylate carbon atoms. These calculations showed significant stabilization when the cation was present (for details see Supporting Information).
39. For details see the Supporting Information.
40. G. M. Sheldrick, SHELXS-97, Programs for Crystal Structure Determination, University of Göttingen, 1997.